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Mechanisms of reactions of BH_2^+, $HBOH^+$, and $H_2BOH_2^+$ with H_2O. An experimental gas phase isotope labeling and theoretical ab initio study

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Abstract

The reactions of BH_2^+, $HBOH^+$, and $H_2BOH_2^+$ with H_2O have been studied in the gas phase by using a tandem flowing afterglow-selected ion flow tube apparatus. Proton transfer to H_2O has been observed in the reactions with $HBOH^+$ and $H_2BOH_2^+$; addition and elimination of a hydrogen molecule occurs in the reaction with BH_2^+. The mechanisms of these reactions have been elucidated by labeling the reagents with deuterium and ^{18}O isotopes. An alternative pathway for proton transfer from $HBOH^+$ and $H_2BOH_2^+$ to H_2O has been observed, which involves intermediate formation of a boron-oxygen bound adduct and scrambling of oxygen atoms within it. The proposed mechanisms are supported by ab initio theoretical calculations that have been carried out at Moller–Plesset (MP2) (full)/6–311G(d, p) level. Rate constants for the reactions have been measured and found to be close to theoretical collision rates in the gas phase. (Int J Mass Spectrom 179/180 (1998) 55–60) © 1998 Elsevier Science B.V.

Keywords: Borohydride ions; Boron–oxygen bond; Addition-elimination reactions; Isotope labeling; Tandem FA-SIFT

Introduction

We have reported recently that BH_2^+ cation reacts readily with a number of nucleophilic reagents in the gas phase [1]. Previously, we also gave an account of the three-body association reaction of BH_2^+ with H_2 in helium with formation of unusual species BH_4^+ and BH_6^+ [2]. The highly reactive BH_2^+ ion is not known in solution but may be prepared (along with a number of other borohydride ions) in the gas phase under flowing afterglow conditions by electron impact ionization of B_2H_6 [1,2]. In this article we present a detailed mechanistic study of the reaction of BH_2^+ with water by using deuterium and oxygen-18 labeling and ab initio calculations. The product of this reaction, $HBOH^+$, is an important constituent of the flowing afterglow mass spectrum of diborane, [1] because traces of water are always present in the helium buffer gas. As we have shown previously, [1] this ion undergoes further proton transfer reaction with water forming H_3O^+.

Another ion in the spectrum of diborane that can clearly be shown to contain atoms other than boron and hydrogen is $H_2BOH_2^+$, the adduct of BH_2^+ ion and a water molecule. This ion is an important intermediate in the reaction of BH_2^+ with water and its chemistry is also discussed in this article.

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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Experimental

The flowing afterglow-selected ion flow tube (FA-SIFT) instrument and practical details of typical experiments have been described in detail in our previous articles [1–3] and in the excellent overview of flow tube techniques [4]. Therefore, we give here only a brief outline of the apparatus used for this study. It consists of two flow tubes, separated by a quadrupole mass filter and terminated by a quadrupole mass analyzer and electron multiplier ion detector. Small amounts of a 5% mixture of B_2H_6 in helium were introduced into the helium buffer gas of the first flow tube and ions were generated by electron impact and ion-molecule reactions. For the formation of labeled ions, D_2O, $H_2^{18}O$, or D_2 were added as necessary. Ions of the desired mass-to-charge ratio (m/z) were selected by the first quadrupole and injected into the second flow tube where they were allowed to react with vapors of neutral reagents introduced through inlets placed along the tube or, in some instances, with traces of water present in the helium buffer gas. By monitoring the reactive decay of the ion as a function of distance along the reaction tube, kinetic parameters for the process may be deduced. At the end of the reaction flow tube the product ions were sampled into a second quadrupole mass analyzer and detected by the electron multiplier.

High purity helium (99.995%, US Welding, Denver, CO) was used in all experiments. Helium was dried over 3 Å molecular sieves in a tubular coil immersed in liquid nitrogen prior to entering the flow tubes. Diborane was used as a 5% mixture with helium (Matheson). Laboratory distilled water was used after degassing; D_2O, $H_2^{18}O$ enriched water, and D_2 were purchased from Cambridge Isotope Laboratories and used without further purification.

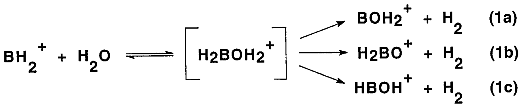
Measured reaction rate constants are reproducible within ±10% or better; we estimate the absolute error as ±20%. Mass discrimination of the ion detector was neglected in branching ratio measurements because the isotopic ions did not differ by more than two m/z units.

Calculations were performed by using Gaussian 94 [5] and Spartan v.4.0 [6] software packages on IBM RS-6000 and SGI Indigo^2 computers, respectively. Geometry optimizations, energy, and vibrational frequency calculations were carried out at MP2(full)/6-311G(d,p) level of theory that, as we showed previously [1], adequately describes structures and relative energies of molecules similar to those studied in this work.

Results and discussion

Reaction of BH_2^+ with water

In the gas phase BH_2^+ (m/z 13) [7] reacts rapidly (rate constant 1.81×10^{-9} cm^3 molecule^{-1} s^{-1}, reaction efficiency 0.7) [8] with water to form an ion of composition H_2BO^+ and dihydrogen. A reasonable mechanism for this process would involve exothermic association to form an adduct with sufficient internal energy to allow loss of H_2. The two hydrogen atoms of H_2 could, in principle, come from the BH_2^+ [Eq. (1a)], from the H_2O Eq. (1b), or one could come from each reactant (1c).



It also seemed possible that the hydrogens in the activated adduct could scramble before hydrogen loss. We decided to investigate the nature of H_2 loss by a deuterium labeling experiment.

The simplest experiment appeared to be to allow BH_2^+ to react with D_2O. In fact, this proved impractical because the reaction is so fast that the inevitable traces of H_2O in the helium buffer gas interfered with the analysis. It therefore was necessary to perform the symmetrical experiment in which BD_2^+ is allowed to react with H_2O. Fortunately, we had previously determined that BH_2^+ will exchange with D_2 in the first flow tube, forming BHD^+ and BD_2^+; the latter ion (m/z 15) can be mass selected and injected cleanly into the reaction flow tube. When reaction with H_2O

occurs, only a single ion, *m*/*z* 30, is produced corresponding to loss of HD [Eq. (2)].

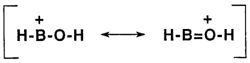
$$BD_2^+ + H_2O \rightleftharpoons \left[D_2BOH_2^+ \right] \longrightarrow DBOH^+ + HD \qquad (2)$$

Thus, the hydrogen (or deuterium) is lost from each heavy atom and there is no scrambling among the atoms in the adduct.

This result was not unexpected because we have found previously that a similar loss of HD occurs in the reaction of BD_2^+ with CH_4 [Eq. (3)] [1].

$$BD_2^+ + CH_4 \rightleftharpoons \left[D_2BCH_4^+ \right] \longrightarrow DBCH_3^+ + HD \qquad (3)$$

In addition, the ion $HBOH^+$ should, on simple resonance and electronic grounds, be the most stable of the three possible ions in Eq. (1).



$$\left[H\text{-}\overset{+}{B}\text{-}O\text{-}H \longleftrightarrow H\text{-}B\text{=}\overset{+}{O}\text{-}H \right]$$

Molecular orbital calculations support these experimental observations and further elucidate the mechanism of the reaction. Fig. 1 represents the optimized molecular structures of intermediates and transition states, Fig. 2 shows the potential energy diagram for the reaction of BH_2^+ with H_2O, and the numerical results of calculations are given in Table 1. The first step of the reaction is formation of the adduct $H_2BOH_2^+$ [structure (1a)]. This process is so exothermic (about 78 kcal mol^{-1}) that the central barrier of over 45 kcal mol^{-1} is easily overcome, and a weakly bound adduct [structure (1c)] is formed in which the H_2 molecule is held at the boron atom by a three-center two-electron bond. This complex represents a minimum on the potential energy surface but our best computational efforts have not located a barrier to its dissociation, which is slightly exothermic. Rapid dissociation of this complex does not allow the three hydrogens at the boron atom to scramble (the barrier for this process is about 15 kcal mol^{-1}) [1], therefore the eliminated H_2 molecule always contains the hydrogen atom that has migrated from the oxygen atom together with one from the boron.

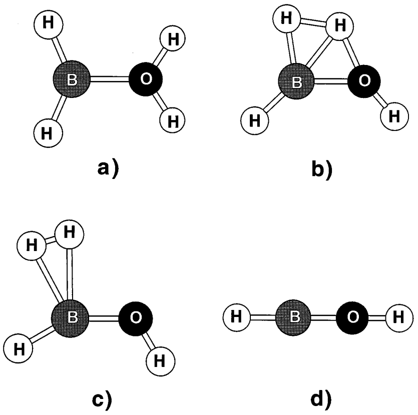


Fig. 1. Molecular structures of species relevant to the reaction of BH_2^+ with H_2O obtained from MP2(full)/6-311G(*d*, *p*) calculations.

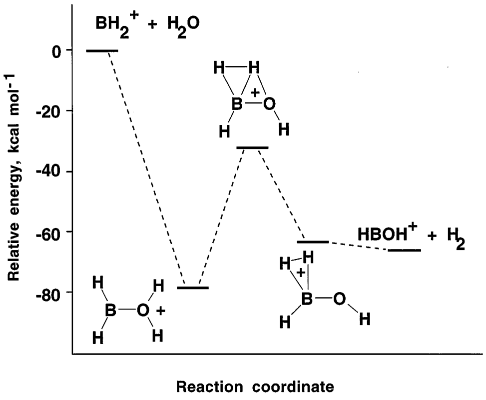


Fig 2. The calculated potential energy profile for the reaction of BH_2^+ with H_2O.

Reaction of HBOH$^+$ with water

The initially formed $HBOH^+$ reacts further with water by proton transfer; in this case, we can envision proton transfer occurring either from oxygen [Eq. (4a)] or boron [Eq. (4b)].

$$HBOH^+ + H_2O \begin{cases} \longrightarrow HBO + H_3O^+ & (4a) \\ \longrightarrow BOH + H_3O^+ & (4b) \end{cases}$$

Table 1
Results of ab initio molecular orbital calculations

Species[a]	Symmetry	MP2(full)/6-311(d, p)	N_{imag}[b]	ZPE[c]
$H_2BOH_2^+$ (1a)	C_{2v}	−101.9666	0	0.0480
H_2BHOH^+ (1b)	C_1	−101.8861	1	0.0413
$HB(H_2)OH^+$ (1c)	C_1	−101.9383	0	0.0415
$HBOH^+$ (1d)	$C_{\infty v}$	−100.7781	0	0.0237
$HBOHOH_2^+$ (5a)	C_s	−177.1349	0	0.0510
$HB(H_2O)OH^+$ (5b)	C_s	−177.1569	0	0.0541
$HB(OH)HOH^+$ (5c)	C_2	−177.1032	1	0.0494
$HB(OH)OH_2^+$ (5d)	C_s	−177.1374	1	0.0538
$H_2BOH_2OH_2^+$ (5e)	C_s	−178.3088	0	0.0713
$H_2B(H_2O)_2^+$ (5f)	C_1	−178.3177	0	0.0768
HBO	$C_{\infty v}$	−100.5150	0	0.0145
BOH	$C_{\infty v}$	−100.4251	1	0.0122
HBO^+	$C_{\infty v}$	−100.0249	0	0.0136
BOH^+	C_s	−100.0924	0	0.0134

[a] Expressions in parentheses refer to the figure number and the structure in that figure. Energies are in hartrees.
[b] Number of imaginary vibrational frequencies.
[c] Zero-point vibrational energy correction from MP2(full)/6-311G(d, p) frequencies, unscaled.

To investigate this process we added traces of H_2O to the first flow tube, mass selected and injected the $HBOH^+$ ion (m/z 29) thus produced into the reaction flow tube, and measured the rate coefficient for its reaction with H_2O. As expected, the reaction is extremely fast, $k = 1.95 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}; efficiency 0.92 [8].

We found a second method for producing $HBOH^+$ for study. If H_2O is added to the first flow tube relatively large amounts of $H_2BOH_2^+$ (m/z 31) are formed. This could be formed by a three-body association reaction between BH_2^+ and H_2O, but because of its relatively large abundance, we believe it is more likely to arise from a chemical reaction, as, for example, that shown in Eq. (5).

$$B_2H_5^+ + H_2O \longrightarrow H_2BOH_2^+ + BH_3 \quad (5)$$

$H_2BOH_2^+$ can be selected and injected into the second flow tube. If the injection energy is increased it undergoes collision induced dissociation (CID) with helium resulting in loss of H_2 and formation of $HBOH^+$.

The development of this synthetic method allowed us to carry out additional tracer experiments. Addition of D_2O to the first flow tube produces $H_2BOD_2^+$ (m/z 33), which can be selected and injected. It, in turn, loses HD upon CID to produce $HBOD^+$ (m/z 30) [Eq. (6)],

$$H_2BOD_2^+ \xrightarrow{\text{CID}} HBOD^+ + HD \quad (6)$$

showing that collisional and chemical activation both lead to HD loss. Subsequent reaction of $HBOD^+$ with water leads exclusively to deuterium transfer [Eq. (7)],

$$HBOD^+ + H_2O \longrightarrow HBO + H_2OD^+ \quad (7)$$

showing that HBO is the neutral product formed. Here, also, the reaction leads to the formation of the more stable products, because calculations show that HBO is more stable than BOH by about 55 kcal mol^{-1}.

We wondered, however, if the proton transfer reaction between $HBOH^+$ and H_2O is as simple as it appears, since $HBOH^+$ is both a Brönsted acid and a Lewis acid at the boron atom. Coordination of the oxygen of H_2O with boron and intramolecular proton transfer could lead to oxygen exchange as well as overall proton transfer. To test for this possibility we

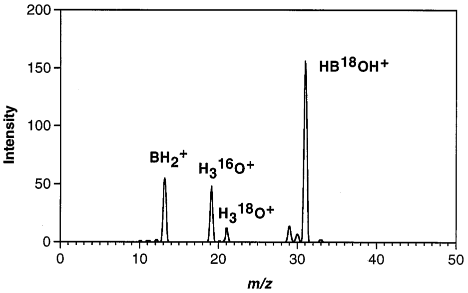
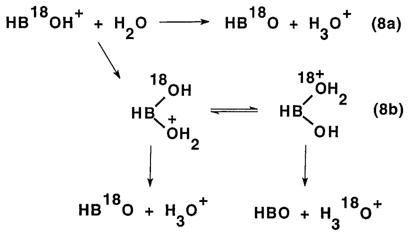


Fig. 3. Mass spectrum obtained in the reaction of $HB^{18}OH^+$ ion with $H_2^{16}O$.

added small amounts of $H_2^{18}O$ to the first flow tube and selected and injected $H_2B^{18}OH_2^+$ (*m/z* 33). CID of this ion produces $HB^{18}OH^+$ (*m/z* 31) that, upon reaction with H_2O, generates both H_3O^+ (80%) and $H_3^{18}O^+$ (20%) (Fig. 3). Therefore, appreciable reaction at boron occurs [Eq. (8b)], in competition with proton transfer without formation of an adduct (Eq. 8a).



The calculated reaction profile for this process is given in Fig. 4 and the relevant optimized molecular structures in Fig. 5. If we assume that the intramolecular proton transfer between the two oxygens is fast compared to dissociation, then half of the adduct will lead to H_3O^+ and half to $H_3^{18}O^+$ and the overall reaction goes 60% by direct proton transfer and 40% by first forming an adduct.

Reaction of $H_2BOH_2^+$ with water

The ion $H_2BOH_2^+$ (*m/z* 31) also reacts rapidly with water to produce H_3O^+ ($k = 1.31 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, efficiency 0.62) [8]. As with $HBOH^+$, two competing processes can be envisioned, direct proton transfer [Eq. (9a)] or prior complexation of oxygen in water to boron [Eq. (9b)]. Again, we used an ^{18}O label to distinguish between these two pathways.

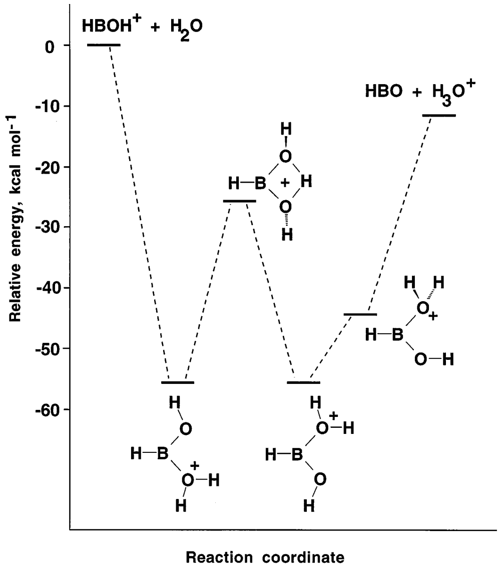


Fig. 4. The calculated potential energy profile for the reaction of $HBOH^+$ with H_2O.

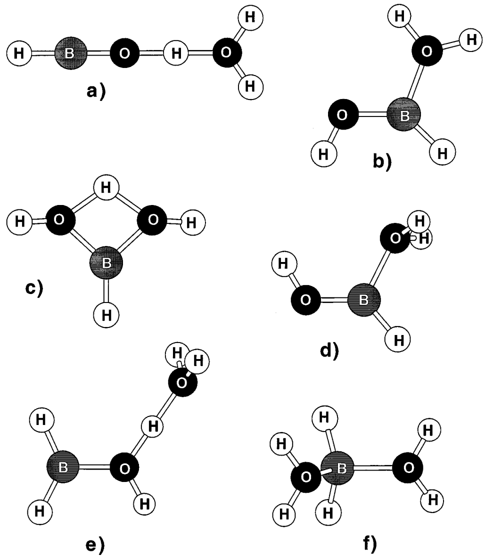
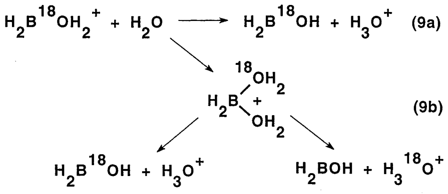


Fig. 5. Molecular structures of species relevant to the reactions of ions $HBOH^+$ and $H_2BOH_2^+$ with H_2O obtained from MP2(full)/6-311G(*d*, *p*) calculations.



If all the reaction occurs by direct proton transfer Eq. (9a), only H_3O^+ will be formed. If all the reaction occurs by prior formation of the symmetrical adduct, a 1:1 mixture of H_3O^+ and $H_3^{18}O^+$ will be formed. When the experiment was carried out, a 2:1 mixture of H_3O^+ and $H_3^{18}O^+$ was formed, showing that about two thirds of the time a symmetrical adduct is formed.

Collision induced dissociation of HBOH$^+$

When $HBOH^+$ is produced by CID of $H_2BOH_2^+$ there is a small amount of further fragmentation by loss of a third hydrogen atom. When $H_2BOD_2^+$ is fragmented, HD loss is followed exclusively by H loss, showing that the resulting radical cation is BOD^+ [Eq. (10)]:

$$HBOD^+ \xrightarrow{CID} BOD^+ + H \qquad (10)$$

Our ab initio calculations confirm that the radical cation $BOH^{+\cdot}$ is more stable that its isomer $HBO^{+\cdot}$ by about 42 kcal mol^{-1}. As we noted above, in the neutral species HBO is more stable than BOH by 55 kcal mol^{-1}. This drastic reversal of stability between neutral and cationic isomers is analogous to that found in the HCN–HNC, HCN^+–HNC^+ system [9], a not unexpected correspondence because the two systems are isoelectronic.

Conclusions

The ion BH_2^+ undergoes a fast reaction with water through the intermediacy of the ion $H_2BOH_2^+$ and yields $HBOH^+$ upon elimination of H_2 molecule. One atom of hydrogen is eliminated from the boron atom, the other from the oxygen.

The ions $H_2BOH_2^+$ and $HBOH^+$, as well as their isotopically labeled counterparts, were generated individually. The proton transfer reactions of these ions with water involve formation of adducts with boron-oxygen bonding and efficient scrambling of the two oxygen atoms prior to dissociation to products.

Collision induced dissociation of $HBOH^+$ leads to formation of the radical cation BOH^+, which is significantly more stable than HBO^+. This is in strong contrast with the stability of neutral species, HBO being much lower in energy than BOH.

Acknowledgement

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References

[1] C.H. DePuy, R. Gareyev, J. Hankin, G.E. Davico, M. Krempp, R. Damrauer, J. Am. Chem. Soc. 120 (1998) 5086.
[2] C.H. DePuy, R. Gareyev, J. Hankin, G.E. Davico, R. Damrauer, J. Am. Chem. Soc. 119 (1997) 427.
[3] (a) J.M. Van Doren, S.E. Barlow, C.H. DePuy, V.M. Bierbaum, Int. J. Mass Spectrom. Ion Processes 81 (1987) 85; (b) S. Gronert, R.A.J. O'Hair, S. Prodnuk, D. Sülzle, R. Damrauer, C.H. DePuy, J. Am. Chem. Soc. 112 (1990) 997; (c) M.S. Robinson, M.L. Polak, V.M. Bierbaum, C.H. DePuy, W.C. Lineberger, ibid. 117 (1995) 6766.
[4] S.T. Graul, R.R. Squires, Mass Spectrom. Rev. 7 (1988) 263.
[5] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, G.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Revision C.2, Gaussian, Inc., Pittsburgh, PA, 1995.
[6] SPARTAN version 4.0, Wavefunction, Inc.
[7] Isotopically pure ion $^{11}BH_2^+$ was used in this study, and BH_2^+ stands for $^{11}BH_2^+$ in all discussions.
[8] Reaction efficiency is a ratio of measured rate constant and theoretical collision rate calculated according to W.J. Chesnavich, T. Su, M.T. Bowers, J. Chem. Phys. 72 (1980) 2641.
[9] (a) S. Petrie, C.G. Freeman, M. Meot-Ner (Mautner), M.J. McEwan, E.E. Ferguson, J. Am. Chem. Soc. 112 (1990) 7121; (b) A. Hansel, Ch. Scheiring, M. Glantschnig, W. Lindinger, E.E. Ferguson, J. Chem. Phys. (in press).